



Short communication

A novel composite cathode for intermediate temperature solid oxide fuel cell

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HIGHLIGHTS

- $\text{Ni}_{0.79}\text{Co}_{0.2}\text{Zn}_{0.01}\text{O}$ (NCZ) – SDC composite was firstly evaluated as cathode for IT-SOFC.
- The output power has been further improved by partial substituting Li for Ni at Ni sites.
- At 600 °C, the cell $\text{Ni-SDC|SDC|Li}_{0.2}\text{Ni}_{0.79}\text{Co}_{0.2}\text{Zn}_{0.01}\text{O}_2$ showed the peak power density of 0.98 W cm^{-2} .

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ABSTRACT

Mixed transition-metal oxide $\text{Ni}_{0.79}\text{Co}_{0.2}\text{Zn}_{0.01}\text{O}$ (NCZ) powders have been prepared by the modified Pechini method and studied as cathode for intermediate-temperature solid oxide fuel cells (IT-SOFCs). The $\text{Ni-Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}(\text{SDC})|\text{SDC}|\text{SDC-NCZ}$ single cell achieves 326 mW cm^{-2} at 600 °C. The output power has been further improved by partial substituting Li for Ni at Ni sites. The $\text{Ni-SDC}|\text{SDC}|\text{SDC-Li}_{0.2}\text{Ni}_{0.79}\text{Co}_{0.2}\text{Zn}_{0.01}\text{O}_2$ (L2NCZ) cell with the SDC film of 30 μm in thickness shows maximum power outputs of 1.32, 0.98 and 0.62 W cm^{-2} at 650, 600 and 550 °C, respectively. The impedance measurements at open circuit conditions show that the overall electrode polarization resistances is 0.033, 0.112, $0.351 \Omega \text{ cm}^2$ at 650, 600 and 550 °C, respectively. The primary results indicate a new family of potential cathode material compatible with the SDC electrolyte for IT-SOFCs.

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1. Introduction

Solid oxide fuel cells (SOFCs) are the most efficient devices yet invented for conversion of chemical fuels directly into electrical power [1,2]. Numerous potential opportunities exist for using SOFC system at various power levels, ranging from portable power sources and as auxiliary units in vehicles, to large-scale power stations [3,4]. Recently their potential application as electricity storage devices has also attracted attention [5–7]. The real-world efficiency of SOFC is largely determined by the activation of oxygen reduction reactions (ORR) on the cathodes. However, poor cathodic performance at intermediate temperature has become the main obstacle to the commercial application.

Mixed transition-metal oxides in $(\text{A}, \text{B})\text{O}_x$ ($\text{A}, \text{B} = \text{Co}, \text{Ni}, \text{Fe}, \text{Zn}, \text{Mn}$, etc.) composition spaces are among the most active ORR catalysts [8,9]. These oxides have been widely applied in energy storage devices, such as lithium-ion batteries [10], electrochemical

capacitors [11], and metal- O_2 batteries [12], because the presence of mixed valences in these oxides is highly beneficial for ORR by providing donor–acceptor chemisorption sites for the reversible adsorption of oxygen [13,14]. Recently, electrodes based on ZnO/NiO composition were proven to be extremely efficient for low-temperature SOFCs [15]. In particular, ZnO/NiO has been used as the cathode and anode material in a symmetrical configuration, and an excellent fuel cell performance, e.g. a maximum power density of 1107 mW cm^{-2} , has been obtained at 500 °C. Lithiated transition-metal oxide composite has also been extensively studied by many research groups as cathode materials for SOFCs with excellent fuel cell performances [16–19]. However, these mixed transition-metal oxides as cathode materials for SOFCs have not attracted enough research interest. In this communication, as a first study, we investigated the performance of $\text{Ni}_{0.79}\text{Co}_{0.2}\text{Zn}_{0.01}\text{O}$ (NCZ)-SDC as cathode for SOFCs.

2. Experimental

$\text{Ni}_{0.79}\text{Co}_{0.2}\text{Zn}_{0.01}\text{O}$ (NCZ) powders were synthesized by the modified Pechini method with citrate and ethylenediamine

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tetraacetic acid (EDTA) as parallel complexing agents. Proper amounts of chemical reagents of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with the stoichiometric cations of Ni:Co:Zn 0.79:0.2:0.01 were dispersed into deionized water under stirring. EDTA and citric acid were then added to the solution at a mole ratio of total metal ions: EDTA: citric acid of 1:1:1.5. NH_4OH was applied to adjust the pH value of the solution to be around 6.0, and the solution became transparent immediately. Evaporation water on a hot plate, a gel was formed, and then combusted to obtain primary powder, which was subsequently, calcined at 900°C about 2 h to obtain NCZ powders. To prepare $\text{Li}_{0.2}\text{Ni}_{0.79}\text{Co}_{0.2}\text{Zn}_{0.01}\text{O}_2$ (L2NCZ) powders, the aforementioned NCZ was reacted with lithium carbonate by solid-state reaction. A stoichiometric ratio of 0.21:1 = Li: NCZ was taken for the reactions. Both powders were mixed in absolute ethanol using mortar and pestle, and the mixture was annealed at 900°C for 3 h under air. $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC) electrolyte material was prepared with commercially available chemicals of CeO_2 and Sm_2O_3 . Powders of L2NCZ and SDC with a weight ratio of 3:2 were well mixed, pressed into a pellet, and calcined at 1050°C for 3 h. All the starting chemicals are analytical reagents from Sinopharm Chemical Reagent Co., Ltd.

The anode-supported SDC bi-layer was prepared by a dry-pressing method [20,21]. Commercial NiO (99.0%, Sinopharm Chemical Reagent Co., Ltd) and SDC (0.6: 0.4 by weight) powders were mixed and ground with alcohol for 2 h. After the alcohol was evaporated; the dried powder was pre-pressed into discs in a stainless-steel die at 200 MPa as the substrate about 1 mm. Then loose SDC powder, calcined at 700°C for 3 h, was uniformly distributed on to the anode substrate, co-pressed at 300 MPa and sintered subsequently at 1400°C for 3 h in air to densify the SDC membrane. Fine NCZ or L2NCZ powder, calcined at 900°C , was mixed thoroughly with a 40 wt.% SDC and an appropriate amount of terpeneol binder to prepare the cathode slurry, which was painted on the SDC electrolyte membrane, and fired at 1050°C for 2 h in air to form a single cell. Surface of the cathode (L2NCZ-SDC) was covered with a layer of L2NCZ powders in order to prevent the evaporation of Li_2O at the high temperatures. The electrode active area was 0.33 cm^2 . Ag paste was applied as a current collector for both the anode and cathode. Electrochemical measurements of the fuel cell were performed in a ceramic tube with an inner diameter of 10 mm placed inside a furnace. Humidified hydrogen (3% H_2O) was fed to the anode chamber at a flow rate of 100 ml min^{-1} , and air flowed over the cathode surface at a rate of 200 ml min^{-1} . Open circuit voltage and J - V curves were collected using digital multi-meters (XIELI, DPM) based on a two-chamber configuration.

The phase structure of the composite oxides was determined by room-temperature X-ray powder diffraction (XRD) using an X-ray diffractometer (Rigaku Ultima IV) with filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$). Scanning electron microscopy (SEM, JEOL JSM-7500F) was used to characterize the microstructure of the cell after performance test. Electrochemical impedance spectra (EIS) of the fuel cell over the temperature range of 550 – 700°C was performed on a PARSTAT 2273 with frequency range of 0.1 Hz – 100 kHz , and the AC amplitude was 10 mV .

3. Results and discussion

Shown in Fig. 1 are the XRD patterns of NCZ and a L2NCZ-SDC mixture after calcination at 1050°C and SDC are also shown for comparison. As can be seen in Fig. 1, a single phase of NCZ is obtained. Lattice constant of NCZ ($Fm\bar{3}m$) is determined to be $a = 4.177 \pm 0.006\text{ \AA}$ in cubic setting by a least square method. The XRD pattern of L2NCZ calcined at 900°C for 3 h in air shows the formation of a single phase $\text{Li}_{0.4}\text{Ni}_{1.6}\text{O}_2$ (JCPDS card No. 81-0095). The XRD pattern of L2NCZ can be clearly indexed as the NiO phase

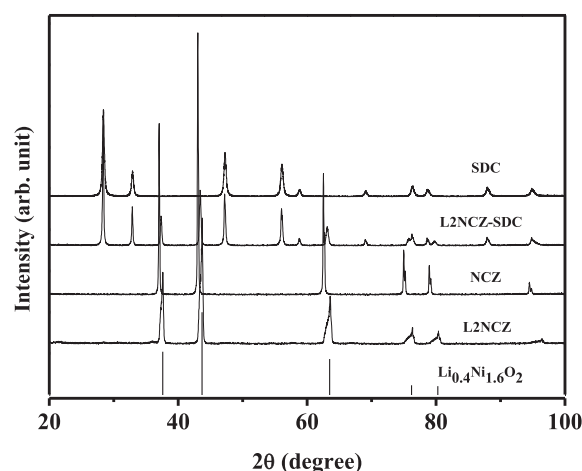


Fig. 1. XRD patterns of NCZ, SDC, and L2NCZ-SDC mixtures after calcination at 1050°C for 3 h.

structure; moreover, it is evident that the peaks corresponding to L2NCZ were shifted to right comparing with NCZ, suggesting that Li have doped into NCZ successfully. The replacement of one Ni^{2+} ion by one Li^+ ion is accompanied by a simultaneous change of valency from Ni^{2+} to Ni^{3+} . The ionic radii of octahedral coordinated Ni^{2+} , Ni^{3+} , and Li^+ is 0.069, 0.056, and 0.076 nm , respectively [22]. The sum of Li^+ and Ni^{3+} radii is 0.132 nm , smaller than the sum of two Ni^{2+} (0.138 nm), which leads to the volume of the unit cell in L2NCZ ($Fm\bar{3}m$, $a = 4.143 \pm 0.002\text{ \AA}$) reduced. To investigate the compatibility between L2NCZ and SDC, a mixture of L2NCZ and SDC powders (weight ratio of 3:2) was fired at 1050°C for 3 h. Fig. 1 also has shown the XRD patterns of a L2NCZ-SDC mixture after calcination at 1050°C . No additional diffraction peaks are observed, indicating that the L2NCZ is chemically compatible with the SDC electrolyte at 1050°C for 3 h.

Fig. 2 shows a SEM micrograph of the cross section of the typical cell after the electrochemical test under H_2 . The composite cathode demonstrates good attachment to the electrolyte without any sign of cracking and delamination, indicating good thermal compatibility between the materials. In this case, the thickness of the cathode layer is about $25\text{ }\mu\text{m}$ whereas the SDC electrolyte film is

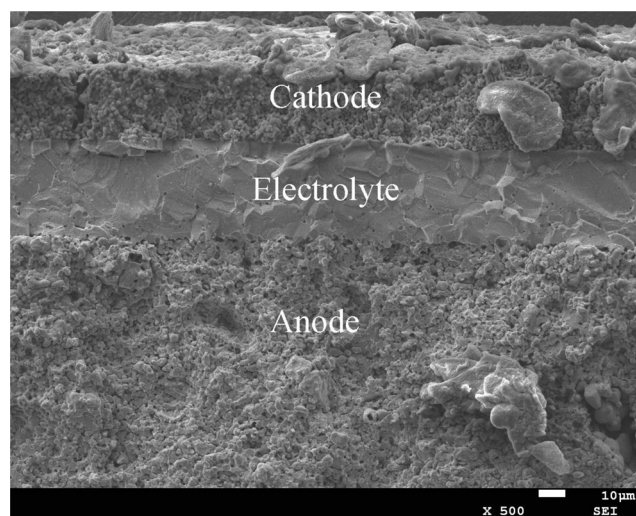


Fig. 2. A typical microstructure of a three-layer anode-supported SDC thin membrane fuel cell.

about 30 μm thick. It is also apparent that the electrolyte presents high density and the electrodes exhibit a porous microstructure with small pores.

The current density–voltage (J – V) characteristics and the corresponding power densities of a fuel cell with the NCZ composite cathode in an anode supporting a $\sim 28 \mu\text{m}$ thick SDC electrolyte fuel cell were investigated at temperatures from 550 to 700 $^{\circ}\text{C}$. As shown in Fig. 3(a), the open-circuit voltage (OCV) of 0.753 and 0.741 V were obtained at 650, and 700 $^{\circ}\text{C}$, respectively. The deviated OCVs from the theoretical value (1.13 V at 650 $^{\circ}\text{C}$) could attribute to the electronic conductivity of doped-ceria induced by the reduction of Ce^{4+} to Ce^{3+} in reducing atmospheres [23]. The lower OCV will decrease the power density of the cell. The peak power density of the cell is 898, 584, 326 and 155 mW cm^{-2} at 700, 650, 600 and 550 $^{\circ}\text{C}$, respectively. Fig. 3(b) shows the impedance spectra of the cell measured at temperature 550–700 $^{\circ}\text{C}$ under open circuit conditions. The intercept with the real axis at high frequencies represents the resistance of the cell, whereas the difference between the high-frequency and low-frequency intercepts with the real axis represents the sum of the electrode interfacial resistances $R_p(a+c)$ of the cell, consists of the contribution from both cathode and anode. The Nyquist plot of the impedance data showed that $R_p(a+c)$ was 0.046, and 0.294 $\Omega \text{ cm}^2$ at 700, and 600 $^{\circ}\text{C}$, respectively. Although we first demonstrate that the Ni-SDC|SDC|SDC-NCZ single cell can be operated with the power output, these values of P_{max} at each temperature point are not

satisfying. Notably, the $R_p(a+c)$ at 600 $^{\circ}\text{C}$ is larger at comparable temperature, e.g., 0.102 $\Omega \text{ cm}^2$ for $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ – $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ [24], 0.048–0.079 $\Omega \text{ cm}^2$ for Ag-modified $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (Ag/BSCF) composite [25], 0.07 $\Omega \text{ cm}^2$ at 650 $^{\circ}\text{C}$ for $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ – $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (SCC/LSGM) hybrid reported by Han et al. [26]. It indicates that the performance of the cell is primarily limited by the high polarization resistance of the electrodes. Considering that when Li^+ partially substitute the normal sites of Ni^{2+} , a hole is introduced in the form of Ni^{3+} or O^- to keep charge neutrality condition, and the oxide becomes a semiconductor, and the electrical conductivity increases in a remarkable way [27–29]. Moreover, $\text{Li}_x\text{Ni}_{1-x}\text{O}$ enjoys wide applications as the electrode for fuel cells, due to its high electrical conductivity together with good oxygen exchange kinetics [16,30]. A Li-doped NCZ (L2NCZ)-SDC composite cathode has been made on the SDC electrolyte, and the performances of the cell Ni-SDC|SDC|SDC-L2NCZ are investigated from 550 $^{\circ}\text{C}$ to 700 $^{\circ}\text{C}$.

The voltages and the corresponding power densities are expressed in Fig. 4(a) as a function of current density. The peak power density of the cell is 1.62, 1.32, 0.98 and 0.62 W cm^{-2} at 700, 650, 600 and 550 $^{\circ}\text{C}$, respectively. Fig. 4(b) shows the impedance spectra of the cell measured at temperature 550–700 $^{\circ}\text{C}$ under open circuit conditions. The plot consists of a large high-frequency arc at $\approx 1.7 \text{ kHz}$ and a small low-frequency arc at $\approx 25 \text{ Hz}$, which can be attributed the charge transfer reaction and oxygen surface exchange on the interfaces. The Nyquist plot of the impedance data

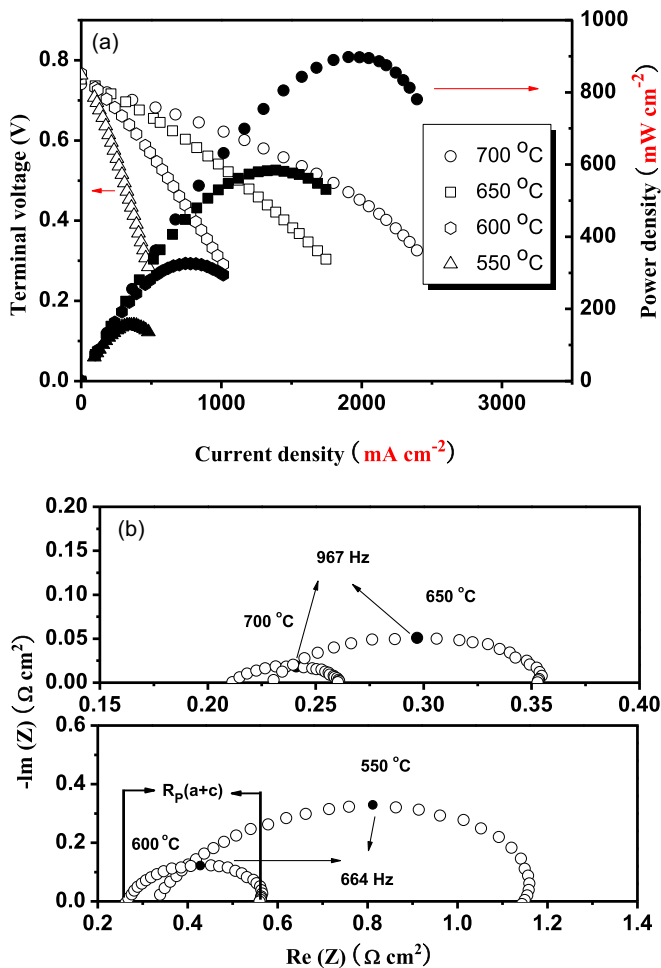


Fig. 3. The performance of single cell: Ni-SDC|SDC|SDC-NCZ ($\sim 28 \mu\text{m}$) (a) J – V and J – P curves and (b) corresponding impedance spectroscopy under OCV conditions.

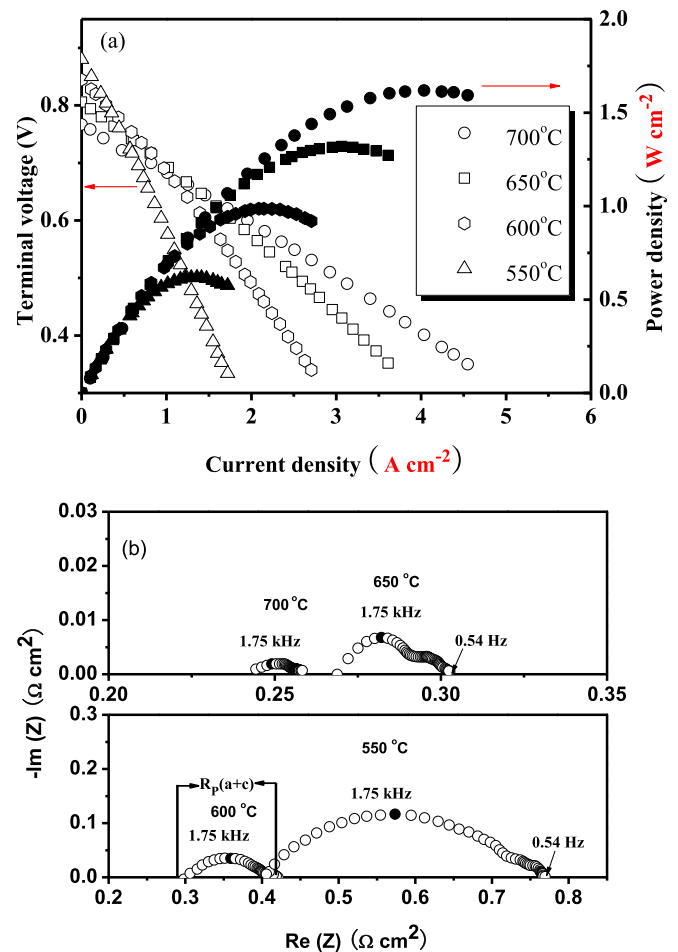


Fig. 4. The performance of single cell: Ni-SDC|SDC|SDC-L2NCZ ($\sim 30 \mu\text{m}$) (a) J – V and J – P curves and (b) corresponding impedance spectroscopy under OCV conditions.

showed that the $R_p(a + c)$ value is 0.012, 0.033, 0.112, 0.351 $\Omega \text{ cm}^2$ at 700, 650, 600 and 550 °C, respectively. These $R_p(a + c)$ values are significantly lower than the NCZ-SDC composite cathode and lithiated NiO cathode [16]. This indicates that the L2NCZ oxide is a promising candidate as a cathode material for SOFCs based on SDC electrolyte.

4. Conclusions

In summary, mixed transition-metal oxide $\text{Ni}_{0.79}\text{Co}_{0.2}\text{Zn}_{0.01}\text{O}$ (NCZ) as cathode material for SOFCs has successfully been developed, and for the first time used in IT-SOFCs. The Ni-SDC|SDC|SDC-NCZ single cell achieves 326 mW cm^{-2} at 600 °C. The output power has been further improved by partial substituting Li for Ni at Ni sites, and the Ni-SDC|SDC|SDC-L2NCZ single cell exhibits the low total polarization resistance at measured temperatures. The maximum power density of the cell reaches 1.62 and 0.98 W cm^{-2} at 700 and 600 °C, respectively, which is much higher than that obtained on the lithiated NiO composite cathode [16]. The primary results indicate that L2NCZ-SDC is a very promising new cathode material for IT-SOFCs.

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